

# Heat capacity of mesoscopically disordered superconductors: implications to MgB<sub>2</sub>

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Electronic heat capacity  $C(T)$  was calculated for a mesoscopically disordered  $s$ -wave superconductor treated as a spatial ensemble of domains with a continuously varying superconducting properties. The domains are assumed to have sizes  $L > \xi_0$ , where  $\xi_0$  is the coherence length. Each domain is characterized by a certain critical temperature  $T_{c0}$  in the range  $[0, T_c]$ . The averaging over the superconducting gap distribution leads to  $C(T) \sim T^2$  for low  $T$ , whereas the specific heat anomaly at  $T_c$  is substantially smeared. The results explain well the  $C(T)$  data for MgB<sub>2</sub>, where a multiple-gap structure is observed.

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An unexpected discovery of relatively high-temperature, high- $T$ , superconductor MgB<sub>2</sub> with a critical temperature  $T_c \approx 40$  K<sup>1</sup> have cast a considerable doubt on the validity of the opinion that high  $T_c$ 's are appropriate to substances with a spin-fluctuation-driven Cooper pairing and, consequently, with a predominantly  $d_{x^2-y^2}$ -wave symmetry of the superconducting order parameter. Indeed, an obvious absence of magnetic ions, a considerable isotopic effect<sup>2</sup>, and Bardeen-Cooper-Schrieffer-like (BCS-like) coherent peaks in optical conductivity<sup>3</sup> and spin-lattice relaxation<sup>4</sup> are indicative of the conventional  $s$ -wave pairing in MgB<sub>2</sub>. As for the electron-phonon background of superconductivity, it also seems highly probable, although a fairly exotic multiple-gap scenario is needed to reconcile the available data (see, e.g., Ref. 5). It is very remarkable that the multiple-gap conventional Cooper pairing is directly found in a number of point-contact, tunneling and Raman measurements<sup>6</sup>. It is even more important that the distribution of gaps may be rather broad<sup>7</sup> and spatially-resolved<sup>8</sup>, although much controversy exists over the number and widths of gaps in the electron density of states (DOS).

In actual truth, the order parameter symmetry for MgB<sub>2</sub> is not unambiguously determined. The low- $T$ , asymptotics of the magnetic field penetration depth  $\lambda(T)$  was shown by muon spin-rotation<sup>9</sup> and optical<sup>3</sup> measurements to be a power-law one. This was interpreted as either an unconventional superconductivity or at least as a highly anisotropic  $s$ -wave pairing. Thermodynamic measurements might be decisive in determining the low- $T$  symmetry-based superconducting properties of MgB<sub>2</sub> because the minority phases or grain boundaries do not affect the results substantially in contrast to, e.g., transport phenomena. The electronic heat capacity,  $C(T)$ , behavior near  $T_c$  is also of great importance to elucidate the nature of superconductivity here. And, indeed, there were a lot of specific heat investigations for MgB<sub>2</sub> performed by various groups<sup>10</sup>.

The main features of the data for  $C(T)$  are (i) small

values of the phase transition anomaly  $\Delta C = C_s - C_n$  at  $T_c$ <sup>10-13</sup> in comparison to the BCS case<sup>14</sup>, when the ratio  $\mu = \Delta C / [\gamma_S(T_c)T_c]$  is equal to  $\mu_{\text{BCS}} = 12/[7\zeta(3)]$ ; and (ii) deviations from the asymptotic BCS behavior at  $T \ll T_c$

$$C_s^{\text{asympt}}(T) = N(0) \left( \frac{2\pi\Delta_0^5}{T^3} \right)^{1/2} \exp\left(-\frac{\Delta_0}{T}\right). \quad (1)$$

Here  $\gamma_S$  is a Sommerfeld constant, the subscripts  $s$  and  $n$  correspond to the superconducting and normal states, respectively,  $N(0)$  is the electron DOS at the Fermi level,  $\Delta_0$  is the energy gap value at  $T = 0$ ,  $k_B = \hbar = 1$ . The deviations from Eq. (1) may be twofold: power-law-like  $\sim T^{211}$  and of the form  $\sim \exp(-\frac{A}{T})$ <sup>13,15</sup>, where the constant  $A$  is much less than  $\frac{\pi}{\gamma}T_c \approx 1.76 T_c$ , as it should be in the weak-coupling superconductor<sup>14</sup>,  $\gamma = 1.78 \dots$  is the Euler constant. Thus, the raw specific heat data do not give definite answers to the problems of the order parameter symmetry and the underlying mechanisms of superconductivity.

In this article on the basis of the experimentally proved *distribution* of energy gaps we show that *both* main features of  $C_s(T)$  can be explained by the conventional  $s$ -wave superconductivity, so that these data can be easily reconciled with other observations<sup>3,4</sup>. The adopted approach, being the outgrowth of the earlier one<sup>16</sup>, is phenomenological because the origin of the gap distribution is not known precisely. However, in accordance with tunneling data<sup>8</sup>, the gap distribution is considered to occur *in the real space* rather than in the  $\mathbf{k}$ -space, as was suggested, e.g., in Refs. 10,11. The theoretical description of such spatially disordered superconductors depends on the ratio between the characteristic superconducting domain size  $L$  and the coherence length  $\xi_0$ <sup>17</sup>. If  $L > \xi_0$ , superconducting properties are determined by local values of the order parameter  $\Delta$ . In the case of MgB<sub>2</sub> there is a large scatter of  $\xi_0$ , inferred from different experiments and for *different kinds* of samples<sup>6</sup>, so that we may estimate this quantity as lying in the range from 25 Å to

65 Å. This dispersion of  $\xi_0$  qualitatively correlates with the broad spectra of gaps in tunnel and point-contact spectra<sup>8,7,10,6</sup>.

Let us examine a  $T$ -independent configuration of mesoscopic domains, with each domain having the following properties:

(A) at  $T = 0$  it is described by a certain superconducting order parameter  $\Delta_0 \leq \Delta_0^{\max}$ ;

(B) up to a relevant critical temperature  $T_{c0}(\Delta_0) = \frac{\gamma}{\pi}\Delta_0$ , it behaves like an isotropic BCS superconductor, i.e. the superconducting order parameter  $\Delta(T)$  is the Mühlischlegel function  $\Delta(T) = \Delta_{\text{BCS}}(\Delta_0, T)$ <sup>14</sup>; and the electronic specific heat is characterized in this interval by the function  $C_s(\Delta, T)$ ;

(C) at  $T > T_{c0}$  it transforms into the normal state, and the relevant property is  $C_n(T)$ .

At the same time, the values of  $\Delta_0$  scatter for various domains. The current carriers move freely across domains and inside each domain acquire appropriate properties. The adopted picture is especially suitable for superconductors with small coherence lengths  $\xi_0$ <sup>10</sup>.

In other words, each domain above its  $T_{c0}$  is in the normal phase and its specific heat is<sup>14</sup>

$$C_n(T) = \frac{\pi^2}{3}N(0)T. \quad (2)$$

For simplicity we restrict ourselves to the situation when the whole sample above  $T_c$  is electronically homogeneous, i.e. is characterized by a common approximately constant  $N(0)$  value. Below  $T_{c0}$  for a given mesoscopic domain, a corresponding isotropic gap appears on the Fermi surface. The microscopic background of the assumed scatter in  $T_{c0}$ 's may be diverse but ultimately manifests itself as a variation either of the electron-phonon interaction magnitude or of local values of the Coulomb pseudopotential.

In the framework of our phenomenological approach, superconductivity (if any) inside a chosen domain is described by the relevant parameters  $\Delta_0$  and  $T_{c0}$ . They are bounded from above by  $\Delta_0^{\max}$  and  $T_c$ , respectively. These  $\Delta_0$ 's may or may not group around a certain crowding value  $\Delta_0^*$  depending on the sample texture. The existence of such two possibilities is in accordance with the varied data for  $\text{MgB}_2$ <sup>8,7,10,6,18</sup>. The specific gap distribution is described by the function  $f_0(\Delta_0)$ .

Thus, for all  $T$  in the interval  $[0, T_c]$ , where  $T_c = \max T_{c0}$ , the superconducting sample consists of superconducting (s) and nonsuperconducting (n) grains more or less homogeneously distributed over the sample volume.

The measured  $C_s(T)$  is an averaged sum of contributions from both phases

$$\langle C(T) \rangle = \langle C_n(T) \rangle + \langle C_s(T) \rangle, \quad (3)$$

which depends on the distribution function  $f(\Delta, T)$  of superconducting domains, and on the fraction  $\rho_n(T)$  of the normal phase<sup>16</sup>

$$\langle C_n(T) \rangle = C_n(T)\rho_n(T), \quad (4)$$

$$\langle C_s(T) \rangle = \int_0^{\Delta^{\max}(T)} C_s(\Delta, T) f(\Delta, T) d\Delta. \quad (5)$$

Here  $\Delta^{\max}(T) = \Delta_{\text{BCS}}(\Delta_0^{\max}, T)$  and  $f(\Delta, T)$  is a result of the thermal evolution of the initial (at  $T = 0$ ) distribution function  $f_0(\Delta_0)$ . It is convenient to normalize all temperatures by  $T_c$  and all energy parameters by  $\Delta_0^{\max}$ :  $t = T/T_c$ ,  $\delta = \Delta/\Delta_0^{\max}$  with relevant indices retained, and to consider  $C_s(T)$  and  $C_n(T)$  together with their averaged counterparts, normalized by the  $C_n(T_c)$  value, i.e.,  $c_{s,n}(t) = C_{s,n}(T)/C_n(T_c)$ . Then one can easily find that for each domain, characterized by the parameter  $\delta_0$  at  $t = 0$ , the dimensionless heat capacity is either

$$c_n(t) = t, \quad t > \delta_0 \quad (6)$$

or

$$c_s(t) = \delta_0 c_{\text{BCS}}\left(\frac{t}{\delta_0}\right), \quad t < \delta_0, \quad (7)$$

where  $c_{\text{BCS}}(x)$  is a well-known normalized heat-capacity function for a standard BCS superconductor<sup>14</sup>. For a surmised domain ensemble a distribution function  $f(\Delta, T)$  for finite  $T$  is defined by the formula

$$f(\Delta, T) d\Delta = f_0(\Delta_0) d\Delta_0. \quad (8)$$

Then the dimensionless heat capacity takes the form

$$\langle c_s(t) \rangle = \int_t^1 c_{\text{BCS}}\left(\frac{t}{\delta_0}\right) f_0(\delta_0) \delta_0 d\delta_0. \quad (9)$$

Introducing a new variable  $z = t/\delta_0$  and expanding the function  $f_0(t/z)$  into a series we arrive at the proper low- $t$  asymptotics

$$\langle c_s(t \rightarrow 0) \rangle = t^2 \int_0^1 \frac{dz}{z^3} f_0(0) c_{\text{BCS}}(z) \approx 2.45 f_0(0) t^2. \quad (10)$$

The  $t$ -dependence of the next term in the expansion for  $\langle c_s(t) \rangle$  can be estimated in the limit  $t \rightarrow 0$  by substitution of the normalized expression (1) for  $c_{\text{BCS}}(z)$ . It turns out that this expression decreases as  $O[t^{5/2} \exp(-\frac{\pi}{\gamma t})]$ .

Now, in the same low- $T$  region let us take a look at the contribution  $\langle c_n(t) \rangle$  of the continuously expanding normal phase. At any  $T$ , all domains with  $\Delta_0 < \frac{\pi}{\gamma}T$  (i.e.  $\delta_0 < t$ ) are nonsuperconducting, with the total normal phase fraction being

$$\rho_n(t) = \rho_n(0) + \int_0^t f_0(\delta_0) d\delta_0. \quad (11)$$

For simplicity, below we restrict ourselves to the case when all domains at  $t = 0$  are superconducting, i.e.

$\rho_n(0) = 0$ . A generalization to the case  $\rho_n(0) \neq 0$  is obvious: at each temperature there exists an additional contribution from the normal phase. Then the function  $f_0(\delta_0)$  should be normalized by  $1 - \rho_n(0)$ , and all averaging-driven effects would accordingly decrease. Moreover, if  $\rho_n(0) \neq 0$ , the observed heat capacity  $\langle c(t) \rangle$  must include an extra linear contribution  $\rho_n(0)t$  in the true superconducting state exhibiting the Meissner effect.

As for the second term in Eq. (11), the approximation of  $f_0(\delta_0)$  by its limiting value  $f_0(0)$  demonstrates that the main temperature-dependent contribution to  $\rho_n(t)$  is *linear* in  $t$ . Since  $c_n(t)$  is also a linear function of  $t$ , the apparent contribution  $\langle c_n(t) \rangle$  of the normal phase to the resulting specific heat  $\langle c(t) \rangle$  is quadratic in  $t$  for small  $t$ , similarly to  $\langle c_s(t) \rangle$ . Thus, in the suggested model of the disordered superconductor with a broad continuous spatial distribution of domains, possessing different  $T_c$ 's, normal and superconducting contributions to thermodynamical quantities are *functionally indistinguishable* from each other.

In addition to the low- $T$  asymptotics the overall  $T$ -dependence of the heat capacity  $C$  up to  $T_c$  is also of considerable interest. Especially important is to trace the smearing of the anomaly  $\Delta C$  by the *same* effect of disorder which leads to the transformation of the intrinsic exponential low- $T$  behavior of  $C_s(T)$  into a power-law one. These objectives were met by numerical calculations.

For this purpose, a Gaussian model distribution function  $f_0^G(\delta_0)$  was used:

$$f_0^G(\delta_0) \propto \exp \left[ -\frac{(\delta_0 - \delta_0^*)^2}{2d^2} \right]. \quad (12)$$

The parameter  $\delta_0^*$  designates the peak position, which may vary from 0 to 1. By changing the parameter  $d$  we control the dispersion of the domain superconducting properties. Nevertheless, for any  $d$  the function  $f_0^G(\delta_0)$  does not vanish in the limit  $\delta_0 = 0$  and its Taylor series begins with a constant as the main term. Only for highly improbable distribution functions, when simultaneously  $f_0(\delta_0)$  extends to  $\delta_0 = 0$  and matches the condition  $f_0(\delta_0 = 0) = 0$ , the Taylor series may begin with the next term resulting in the asymptotics  $C_s(T) \sim T^3$ .

In Fig. 1 the dependences  $\langle c(t) \rangle$  are depicted in the panel (a) for  $\delta_0^* = 1$  and different dispersion values  $d$ . A substantial spreading of the anomaly  $\Delta C$  readily seen in Fig. 1 seems quite natural in view of the results for  $\text{MgB}_2$ <sup>10–13</sup>. However, the concomitant superposition of various domain contributions distorts the whole curves  $C_s(T)$  and  $C(T)$ , which is much less trivial. This very superposition leads for low  $T$  to the power-law behavior, the asymptotics of which was analyzed above. The low- $T$  parts of the curves  $\langle c(t) \rangle$  are displayed on the log-log scale in the panel (b). Dotted straight lines correspond to the pertinent  $T^2$ -asymptotics for each curve. It is clear that the validity range of the asymptotics extends

with the increase of  $d$ . Although intervals where the  $T^2$ -approximation holds good exist for any  $d$ , for small  $d$  it is merely of academic interest, because both temperatures and heat capacities become too tiny to be experimentally significant. On the other hand, for higher  $T$  in this case the averaged dependences  $\langle c(t) \rangle$  lie rather close to the exponential curve inherent to the BCS theory (the dashed curve). Such transitional parts of the dependences  $\langle c(t) \rangle$  describe well the exponential low- $T$  behavior for some samples of  $\text{MgB}_2$ <sup>13,15</sup> with smaller exponents than in the BCS case.

For large  $d$ , when the Gaussian distribution function  $f_0^G(\delta_0)$  becomes almost uniform (such a random dense, although quasi-discrete, distribution of gaps was found in point-contact spectra<sup>7</sup>), the quadratic asymptotics are valid at least up to  $t = 0.1$  (for the uniform distribution  $f_0^U(\delta_0) = \text{const}$  the relative error of the  $t^2$ -asymptotics is  $\approx 0.6\%$  at  $t = 0.1$  and  $\approx 5\%$  at  $t = 0.2$ ), which agrees with the measurements<sup>11</sup>. For intermediate  $d$  the experimental data in the relevant  $T$ -range may be satisfactorily represented by power-law curves  $C(T) \sim T^n$  with  $n \geq 2$ .

One can make another important conclusion from the numerical data shown in Fig. 1. A one-parameter fitting explains *both* the smearing of the heat-capacity anomaly at  $T_c$  and the appearance of the power-law asymptotics. The latter reproduces the results appropriate to superconductors with order parameters of  $d_{x^2-y^2}$ -wave<sup>19</sup> or extended  $s$ -wave with uniaxial anisotropy<sup>10,11</sup> symmetry. The patterns displayed in these figures explain well the experimental heat capacity dependences  $C(T)$  for  $\text{MgB}_2$ , which demonstrate power-law behavior for lowest attainable  $T$ <sup>10,11</sup> or above the exponential low- $T$  tail<sup>15</sup>. At the same time, the reduction of the anomaly  $\Delta C$  at  $T_c$  with the increase of  $d$ , traced in Fig. 1(a), adequately describes the  $\Delta C$  magnitudes inferred from the analysis of the observed total heat capacity of  $\text{MgB}_2$ , making allowance for crystal lattice and impurity components. Namely,  $\mu \approx 1.13$ <sup>13</sup>,  $0.82$ <sup>10,11</sup>,  $0.7$ <sup>12</sup>, so that the experimental specific heat jump is substantially smaller than the BCS value  $\mu_{BCS}$ .

To summarize, we presented a phenomenological model of the disordered  $s$ -wave superconductor with a random domain network possessing continuously varying superconducting properties. The characteristic domain size  $L$  is supposed to exceed the superconducting coherence length  $\xi_0$ . The spatially averaged electronic heat capacity  $\langle C(T) \rangle$  is calculated. It is shown that its low- $T$  asymptotics is a power-law one  $\sim T^2$ , whereas the anomaly  $\Delta C$  at  $T_c$  is simultaneously smeared. These are just the features appropriate to the heat capacity of  $\text{MgB}_2$ . Although we do not know the exact nature of the partition into domains in this compound, its very existence undoubtedly manifests itself in Raman, point-contact and tunnel spectra<sup>6–8</sup>. One may speculate that the multiple-gap superconductivity originates from some kind of a phase separation rather than from the existence of several groups of current carriers in the same volume<sup>5</sup>. The presented theory may be also invoked to explain low-

$T$  properties of cuprates<sup>16</sup>, although the microscopical background of the multi-gapness may be quite different in both cases.

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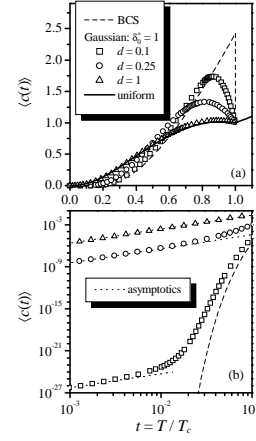


FIG. 1. (a) Temperature dependences of normalized total electronic heat capacity  $\langle c(t) \rangle$  in comparison with the BCS-dependence of superconducting phase fraction. Gaussian distributions with  $\delta_0^* = 1$ . (b) Low-temperature portions of the relevant curves on log-log scale together with their  $t^2$ -asymptotics.